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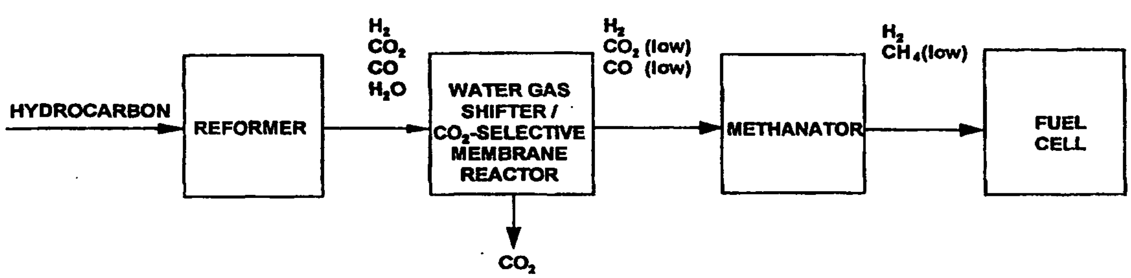
FLOW DIAGRAM FOR THE FIRST CASE OF THE CO_2-SELECTIVE MEMBRANE PROCESS OF THE PRESENT INVENTION



(57) Abstract

The present invention provides a CO_2-selective membrane process that is useful for the purification and/or water gas shift reaction of a reformed gas, generated from on-board reforming of a fuel, e.g., hydrocarbon, gasoline, diesel, methanol or natural gas, to hydrogen for fuel cell vehicles. Another embodiment of the present invention is directed toward a composition comprising a hydrophylic polymer and at least one ammonium halide salt, the ammonium halide salt being present in an amount ranging from about 10 to 80 wt. % based on the total weight of the composition. The composition is suitable in formation of a membrane useful for separating CO_2 from a CO_2-containing gas, particularly from an on-board reformed gas for the CO_2-selective membrane process.

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CO_2-SELECTIVE MEMBRANE PROCESS AND SYSTEM FOR REFORMING A FUEL TO HYDROGEN FOR A FUEL CELL

Field of the Invention

The present invention relates to a membrane process and system for the purification of a fuel, e.g., hydrocarbon, gasoline, diesel, methanol, ethanol or natural gas, to hydrogen for fuel cells. The purification process selectively removes CO_2 from the reformed product thereby enriching the reformed product in H_2 and increasing the H_2/CO_2 ratio. This invention also relates to a polymer composition suitable for forming a membrane that is useful for separating CO_2 from a CO_2-containing gas stream in the purification process. The present invention is particularly useful when the process is carried-out on-board a vehicle using a fuel cell for transportation.

Background of the Invention

Reforming of a fuel, e.g., hydrocarbon, gasoline, diesel, methanol, ethanol or natural gas, to hydrogen is generally proceeded with the formation of the synthesis gas of CO and H_2 first. For example, steam reforming of methanol with a NiO / Al_2O_3 catalyst at 300-400°C (T. B. Su and M. H. Rei, J. Chin. Chem. Soc. (Taipei), 38, 535 (1991)) gives the synthesis gas:

$$CH_3OH \rightarrow CO + 2H_2 \quad (1)$$

Steam reforming of CH_4 with a nickel-based catalyst at 800°C is:

$$CH_4 + H_2O \rightarrow CO + 3H_2 \quad (2)$$

Partial oxidation of CH_4 is:

$$CH_4 + \frac{1}{2}O_2 \rightarrow CO + 2H_2 \qquad (3)$$

Similarly, partial oxidation of other hydrocarbons, e.g., gasoline and diesel, produces the synthesis gas:

$$C_nH_{2n+2} + \frac{n}{2} O_2 \rightarrow n\,CO + (n+1)\,H_2 \qquad (4)$$

where n is an integer. In the partial oxidation, the synthesis gas produced does not contain N_2 when O_2 is used. If air is used instead of O_2, the synthesis gas produced contains N_2.

The synthesis gas is then sent conventionally to two-stage water gas shifters, in which CO is converted to CO_2 via the water gas shift reaction:

$$CO + H_2O \rightarrow CO_2 + H_2 \qquad (5)$$

Typically, the first-stage shifter operates at higher temperature than the second-stage shift, e.g., 373°C for the first stage and 225°C for the second stage. For the water gas shift reaction, CuO / ZnO / Al_2O_3 catalysts can be used. The product gas from steam reforming of methanol under the optimum conditions at 1 atm and 227°C with a water rich feed (water / methanol = 1.5) contains approximately 66% H_2, 21% CO_2, 1% CO, and 12% H_2O (J. C. Amphlett, M. J. Evans, R. A. Jones, R. F. Mann, and R. D. Weir, Can. J. Chem. Eng., 59, 720 (1981)).

In some reforming cases, such as the steam reforming of methanol with a $CuO / ZnO / Al_2O_3$ catalyst, methanol is converted directly and predominantly to CO_2 and H_2:

$$CH_3OH + H_2O \xrightarrow{\text{catalyst}} CO_2 + 3H_2 \tag{6}$$

This reaction operates at temperatures lower than 260°C with methanol conversion as high as 90%; however, trace CO appears at temperatures above 300°C and high methanol conversions of about 90% (C. J. Jiang, D. L. Trimm, and M. S. Wainwright, Appl. Catal. A, 93, 245 (1993)).

Japanese Patents 04,321,502 and 04,325,402 claim processes employing H_2-selective membranes, which selectively pass H_2 and reject other gases, for hydrogen manufacture for fuel cells. However, these processes suffer from a low pressure for the H_2 product gas which is much lower than the pressure for the feed gas. Thus, a compressor is needed to compress the product gas to the pressure of the feed gas. In addition, these processes also usually have other shortcomings, such as low H_2 recovery, large membrane areas, and a high CO_2 concentration in the product gas.

It is an object of the present invention to provide a CO_2-selective membrane process that selectively passes CO_2 over H_2 and other gases and that is useful for the purification and/or water gas shift reaction of a reformed gas, generated from reforming of a fuel, e.g., hydrocarbon, gasoline, diesel, methanol,

ethanol or natural gas, to hydrogen for fuel cells. This CO_2-selective membrane process can be more advantageous than H_2-selective membrane processes in terms of H_2 product pressure (to avoid the need of a compressor for the product gas), H_2 recovery, membrane area, and CO_2 concentration. Another object of the present invention is to provide a novel polymer composition that is suitable in formation of a membrane useful for the CO_2-selective membrane process. Membranes disclosed in U.S. 5,611,843 may also be used for the CO_2 selective membrane process.

Summary of the Invention

The present invention is a process and system to purify a fuel feedstream so that the feedstrean is enriched in H_2. In general, the process includes the steps of reforming the feedstream, and separating CO_2 with a membrane that selectively removes CO_2 from the feedstream. For most fuel feedstreams, a step of water gas shift reaction is also included in the process. The CO_2 selectively permeable membrane may also be used to perform both steps of enhancing water gas shift reaction and separating CO_2. The process further comprises the step of methanating the H_2-enriched feedstream.

If the fuel feedstream is methanol, then a water gas shift reaction step is not necessary. In this embodiment, the CO_2 selectively permeable membrane may be used to perform both steps of reforming and separating.

In a preferred embodiment, the process is carried-out on board a vehicle that uses a fuel cell for transportation.

Another embodiment of the present invention is directed toward a composition comprising a hydrophilic polymer and at least one ammonium halide salt, the ammonium halide salt being present in an amount ranging from about 10 to about 80 wt% based on the total weight of the composition. The composition is suitable in formation of a membrane useful for separating CO_2 from a CO_2-containing gas, particularly from an on-board reformed gas for the CO_2-selective membrane process.

The embodiments of the present invention will become apparent upon a reading of the brief description of the drawings and the detailed description of the invention which follow.

Brief Description of the Drawings

Figure 1 shows the flow diagram for the first case of the CO_2-selective membrane process of the present invention, in which a CO_2-selective membrane is incorporated into the water gas shifter to become the water gas shifter and CO_2-selective membrane reactor for enhancing the conversion of the water gas shift reaction and for purifying the H_2 product via CO_2 removal.

Figure 2 illustrates the flow diagram for the second case of the CO_2-selective membrane process of the present invention, in which a CO_2-selective membrane separator is used to purify the H_2 product from the water gas shift converter.

Figure 3 exhibits the flow diagram for the third case of the CO_2-selective membrane process of the present invention, in which a CO_2-selective membrane is incorporated into the steam reformer for methanol to become the reformer and CO_2-selective membrane reactor for increasing the conversion of the methanol steam reforming reaction and for purifying the H_2 product via CO_2 removal.

Figure 4 shows the flow diagram for the fourth case of the CO_2-selective membrane process of the present invention, in which a CO_2-selective membrane separator is used to purify the H_2 product from the steam reforming of methanol.

Detailed Description of the Invention

The present invention provides a CO_2-selective membrane process that is useful for the purification of a fuel, e.g., hydrocarbon, gasoline, diesel, methanol, ethanol or natural gas, to hydrogen for fuel cells. This process includes reforming the fuel feedstream and separating CO_2 from the feedstream. The CO_2 is removed by contacting a CO_2-containing gas stream with one side of

a nonporous, CO_2 selectively permeable membrane whereby CO_2 is selectively transported over other gases through the membrane and withdrawing from the other side of the membrane a permeate containing CO_2 whereby CO_2 is selectively removed from the gaseous stream. The permeate comprises the CO_2 in increased concentration relative to the feed stream. By "permeate" is meant that portion of the feed stream which is withdrawn at the second side of the membrane, exclusive of other fluids such as sweep gas or liquid which may be present at the second side of the membrane. Air or nitrogen may be used as the sweep gas.

There are four embodiments of the process and the system for performing the process.

In the first case of the present invention, a CO_2-selective membrane is incorporated into the water gas shifter to become the water gas shifter and CO_2-selective membrane reactor for enhancing the conversion of the water gas shift reaction (Eq.(5)) and for purifying the H_2 product via CO_2 removal. Figure 1 shows the flow diagram for the CO_2-selective membrane process of the present invention, consisting of a reformer, a water gas shifter and CO_2-selective membrane reactor, a methanator, and a fuel cell. As shown in this figure, the H_2 product with low CO_2 and CO concentrations is sent to the

methanator, in which CO_2 and CO are converted to CH_4 via the methanator reactions:

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O \quad (7)$$

$$CO + 3H_2 \rightarrow CH_4 + H_2O \quad (8)$$

For enhancing the methanation reactions (Eqs. (7) and (8)), a catalyst of Ru supported on TiO_2 may be used. Finally, the high-purity H_2 product with CH_4 is fed to the fuel cell to drive the electric vehicle. The H_2 product without CO and CO_2 is the most desirable fuel for the fuel cell since CO is a poison for the fuel cell and CO_2 produces CO via the reverse reaction of Eq.(5). To speed up the removal of CO_2 from the permeate side of the CO_2-selective membrane process, a sweep gas, such as air, may be used. The exit stream of the sweep gas may be combined with the anode exhaust stream of the fuel cell to be burned for supplying heat, for example, to the steam reformer or for other heat integration.

The second case of the present invention involves the use of a CO_2-selective membrane separator to purify the H_2 product from the water gas shifter converter. Figure 2 gives the flow diagram for the CO_2-selective membrane process, consisting of a reformer, a water gas shifter, a CO_2-selective membrane separator, a methanator, and a fuel cell.

As mentioned earlier, in some reforming cases, such as the steam reforming of methanol with a CuO / ZnO / Al_2O_3 catalyst, methanol is

converted directly and predominantly to CO_2 and H_2. The third case of the present invention is to incorporate a CO_2-selective membrane into the methanol steam reformer to become the reformer and CO_2-selective membrane reactor for increasing the conversion of the steam reforming reaction (Eq.(6)) and for purifying the H_2 product via CO_2 removal. Figure 3 shows the flow diagram for the CO_2-selective membrane process of this invention, consisting of a reformer and CO_2-selective membrane reactor, a methanator, and a fuel cell.

The fourth case of the present invention uses a CO_2-selective membrane separator to purify the H_2 product from the steam reforming of methanol shown in Eq.(6). Figure 4 illustrates the flow diagram for the CO_2-selective membrane process, consisting of a reformer, a CO_2-selective membrane separator, a methanator, and a fuel cell.

Another embodiment of the present invention is directed toward a composition comprising a hydrophilic polymer and at least an ammonium halide salt, the ammonium halide salt being present in an amount ranging from about 10 to about 80 wt% based on the total weight of the composition and preferably about 40 to about 65 wt%.

The hydrophilic polymers suitable in the practice of the present invention include polyvinylalcohol, polyvinylpyrrolidone, polyethyleneoxide,

polypropyleneoxide, polyacrylamide, polyvinylacetate, blends and copolymers thereof. In general, these polymers will have weight average molecular weights in the range of about 30,000 to 2,000,000 and preferably in the range from about 50,000 to 200,000. Particularly preferred polymers useful in the present invention are polyvinylalcohols having molecular weights in the range from about 50,000 to 150,000.

The ammonium halide salts in the compositions of the present invention are selected from salts having the formulae and mixtures thereof:

$$(R)_4\ N^+ X^-$$

wherein R is hydrogen or an alkyl group having from 1 to 4 carbon atoms and X is a halide, the halide being selected from the group consisting of fluoride, chloride, bromide, iodide, and mixtures thereof.

As previously stated, the amount of ammonium halide salt to be present in the composition is in the range from about 10 to 80 wt% based on the total weight of the composition, and preferably about 40 to about 65 wt%.

The compositions of the present invention are prepared by first forming a solution of the polymer and the ammonium halide salt in a suitable solvent such as water. Generally, the amount of water employed will be in the range from about 70% to 95%. The composition can then be recovered from the

solution by removing the solvent, for example, by allowing the solvent to evaporate; however, it is preferred to use the solution in forming a nonporous membrane. Thus, the resulting solution is formed into a nonporous membrane by techniques well known in the art. For example, the polymer solution can be cast onto a solid support with techniques such as "knife casting" or "dip casting". Knife casting, of course, is a process in which a knife is used to draw a polymer solution across a flat surface to form a thin film of the polymer solution of uniform thickness after which the solvent of the polymer solution is evaporated, at ambient or temperatures up to about 200°C, to yield the fabricated membrane. When, for example, a glass plate is used as the flat surface, the membrane can then be removed from the support providing a free standing polymer membrane. When, alternatively, the flat surface used is a non-selective porous support such as porous polytetrafluoroethylene, the resulting membrane is a composite membrane comprising the selective membrane polymer and the support. Dip casting is the process in which the polymer solution is contacted with a non-selective porous support. Then excess solution is permitted to drain from the support, and the solvent of the polymer solution is evaporated at ambient or elevated temperatures as above. The membrane comprises both the polymer and the porous support.

The membranes of the present invention also may be shaped in the form of hollow fibers, tubes, films, sheets and the like.

In an alternate embodiment of the present invention, a cross-linking agent is added to the polymer and ammonium halide salt solution before forming a membrane from it.

Suitable cross-linking agents include formaldehyde, divinyl sulfone, toluene diisocyanate, glyoxyal, glutaraldehyde, trimethylol melamine, terephthalatealdehyde, epichlorohydrin, vinyl acrylate, and maleic anhyride. Formaldehyde, divinyl sulfone and toluene dissocyanate are particularly preferred.

The amount of cross-linking agent employed will be in the range of about 1 to about 20 wt% based on the total weight of the solid composition formed from the solution.

Membranes formed from the solution containing a cross-linking agent typically are heated at a temperature and for a time sufficient for cross-linking to occur. Generally, cross-linking temperatures in the range from about 80°C to about 200°C are employed. Cross-linking will occur in from about 1 to 72 hours.

As indicated previously, the compositions of the present invention are suitable for use as a nonporous membrane for separating CO_2 from a CO_2-containing gas stream, particularly from an on-board reformed gas for the CO_2-selective membrane process of the present invention.

The present invention will be better understood by reference to the following examples which are offered by way of illustration not limitation.

Examples

In the examples which follow, the separation factor (selectivity) for CO_2 vs. H_2 is expressed as follows:

$$\text{SeparationFactor} = \frac{CO_2 / H_2 \text{ concentration ratio in the permeate}}{CO_2 / H_2 \text{ concentration ratio in the retentate}} \tag{9}$$

The retentate refers to the mixture on the feed side of the membrane which is rejected by the membrane under the operating conditions. Permeability is expressed in Barrer (1 Barrer = 10^{-10} cm^3(STP)·cm/(cm^2·s·cm Hg)). The permeability is determined by the use of the relationship between the permeability P and the permeation rate Q (cm^3(STP)/s) as follows:

$$Q = A\,P\,(p_1 - p_2) / L \tag{10}$$

where A is the membrane area, p_1 and p_2 are the CO_2 partial pressures in the retentate and permeate streams, respectively, and L is the membrane thickness. P/L is called the permeance with a typical unit of GPU (gas permeation unit, 1 GPU = 10^{-6} cm^3(STP)/(cm^2·s·cm Hg)). The partial pressures are determined based on concentration measurements by gas chromatography and total pressure measurements by pressure gauges. The permeation rate is determined based on concentration measurements obtained by gas chromatography and permeate stream flow rate measurements by a flow meter.

Example 1: CO_2-Selective Membrane Process for Purification of a Reformed Gas Containing N_2 at 3 atm

The CO_2-selective membrane process of the present invention is used to purify a reformed gas to supply H_2 to a 10 KW fuel cell with a flow diagram shown in Figure 2 or 4. It should be noted that a fuel cell vehicle may require several 10 KW fuel cells, e.g., 5 (50 KW total). The 10 KW fuel cell requires a hydrogen feed rate of 0.07 mole H_2/s. The reformed gas contains 40% H_2, 19% CO_2, 1% CO, and 40% N_2 (on a water-free basis) at a total pressure of 3 atm. The CO_2-selective membrane used has a CO_2 permeance of 600 GPU, a CO_2 / H_2 selectivity of 75, a CO_2 / CO selectivity of 100, and a CO_2/N_2 selectivity of 100. Air is used as the sweep gas for the permeate to have H_2, CO_2, CO and N_2 partial pressures in the permeate to be insignificant in comparison with their partial pressures in the retentate. By the use of Eq. (10), the membrane area, H_2, CO and N_2 concentrations in the retentate, and H_2 recovery are calculated for a CO_2 concentration of 0.5% in the retentate. The membrane area is 92.5 ft^2, the retentate, i.e., the product gas, has 49.0% H_2, 0.5% CO_2, 1.2% CO, and 49.3% N_2 at a total pressure of 3 atm, and the H_2 recovery is 97.2% of the H_2 available in the reformed gas. The retentate is then treated in a methanator to convert CO_2 and CO to CH_4, resulting in a desirable fuel without containing CO_2 and CO for the fuel cell.

Example 2: CO_2-Selective Membrane Process for Purification of a Reformed Gas Containing N_2 at 10 atm

The CO_2-Selective Membrane Process of the present invention for purification of a reformed gas containing 40% H_2, 19% CO_2, 1% CO, and 40% N_2 (on a water-free basis) at a total pressure of 10 atm is the same as that described in Example 1 except the total pressure. The higher the total pressure (at the same gas composition), the smaller the membrane area. Again, Eq. (10) is used to calculate the membrane area, H_2, CO and N_2 concentrations in the retentate, and H_2 recovery for a CO_2 concentration of 0.5% in the retentate. The membrane area is 27 ft^2, the retentate (product gas) has 49.0% H_2, 0.5% CO_2, 1.2% CO, and 49.3% N_2 at a total pressure of 10 atm, and the H_2 recovery is 97.2% of the H_2 available in the reformed gas. Similarly, the retentate is then treated in a methanator to convert CO_2 and CO to CH_4, yielding a desirable fuel cell fuel without containing CO_2 and CO.

Example 3: H_2 -Selective Membrane Process for Purification of a Reformed Gas Containing N_2 at 10 atm (for comparison)

For comparison, the membrane area and H_2, CO_2, CO and N_2 concentrations in the permeate, i.e., the product gas, for an H_2-selective membrane process with 80% H_2 recovery from the same reformed gas described in Example 2 are calculated in the same way as in Example 2 via Eq. (10) for the 10 KW fuel cell. The membrane process uses a state-of-the-art, commercially available H_2-selective membrane (polyimide) with a H_2 permeance of 100 GPU, a H_2 / CO_2 selectivity of 10, a H_2 / CO selectivity of 100, and a H_2 /N_2

selectivity of 170 (W. S. Winston Ho and Kamalesh K. Sirkar, Membrane Handbook, p. 44, Chapman & Hall, New York (1992)), and this process gives the product gas (permeate) at 1 atm (without the use of a sweep gas). The membrane area is 126 ft^2, and the product gas (permeate) contains 88.3% of H_2, 10.1% CO_2, 0.06% CO, and 1.5% N_2. Table 1 shows the comparison of the CO_2-selective membrane process of the present invention (Example 2) with the H_2-selective membrane process (Example 3). As shown in this table, the membrane process of this invention gives much higher product gas pressure (10 atm vs. 1 atm), greater H_2 recovery (97.2% vs. 80%), and less membrane area required (27 ft^2 vs. 126 ft^2) than the H_2-selective membrane process. In addition, the former process gives a lower combined concentration of carbon oxides in the product gas (0.5% CO_2 and 1.2% CO vs. 10.1% CO_2 and 0.06% CO) than the latter process. The product gas of the former process is suitable for methanation to yield a desirable fuel cell fuel without carbon oxides, whereas the product gas of the latter process has too much CO_2 to be practically suitable for methanation. Therefore, the process of this invention is more effective and advantageous than the H_2-selective membrane process.

Table 1

Comparison of the CO_2-Selective Membrane Process with a H_2-Selective Membrane Process for Purification of a Reformed Gas Containing N_2*

Process	Product Gas Composition (mole %) H_2	CO_2	CO	N_2	Total Product Gas Pressure (atm)	H_2 Recovery (%)	Membrane Area (ft^2)
CO_2-Selective Membrane Process, This Invention (Example 1)	49.0	0.5	1.2	49.3	10	97.2	27
H_2-Selective Membrane Process (Example 3)	88.3	10.1	0.06	1.5	1	80	126

*The reformed gas contains 40% H_2, 19% CO_2, 1% CO, and 40% N_2 at total pressure of 10 atm.

Example 4: CO_2 -Selective Membrane Process for Purification of a Reformed Gas without Containing N_2 at 10 atm

Similar to the process described in Example 1, the CO_2-selective membrane process of the present invention is employed to purify a reformed gas to supply H_2 to a 10 KW fuel cell with a flow diagram shown in Figure 2 or 4. As mentioned earlier, a fuel cell vehicle may require several 10 KW fuel cell, e.g., 5 (50 KW total). The 10 KW fuel cell requires a hydrogen feed rate of 0.07 mole H_2/s. The reformed gas does not contain N_2, and it has a composition of 74.9% H_2, 24% CO_2, and 1.1% CO (on a water-free basis) at a total pressure of 10 atm. The CO_2-selective membrane used, which has a composition of 50 wt% tetramethylammonium fluoride salt and 50 wt% polyvinylalcohol described in Examples 6 and 7, has a CO_2 permeance of 600 GPU and a CO_2/H_2 selectivity of 19. Air is used as the sweep gas for the permeate to have H_2, CO_2 and CO partial pressures in the permeate to be insignificant in comparison with their partial pressures in the retentate. Again, Eq. (10) is used to calculate the

membrane area, H_2 and CO concentrations in the retentate, and H_2 recovery for a CO_2 concentration of 1.2% in the retentate and a CO_2/CO selectivity of 100. The membrane area is 17 ft^2, the retentate (product gas) has 97.1% H_2, 1.2% CO_2, and 1.7% CO at a total pressure of 10 atm, and the H_2 recovery is 83% of the H_2 available in the reformed gas. Again, the retentate is then treated in a methanator to convert CO_2 and CO to CH_4, giving a desirable fuel without containing CO_2 and CO for the fuel cell.

Example 5: H_2-Selective Membrane Process for Purification of a Reformed Gas without Containing N_2 at 10 atm (for comparison)

For comparison, the membrane area and H_2, CO_2 and CO concentrations in the permeate, i.e., the product gas, for a H_2-selective membrane process with 80% H_2 recovery from the same reformed gas described in Example 4 (without containing N_2) are calculated in the same way as in Example 4 via Eq. (10) for the 10 KW fuel cell. The membrane process employs the state-of-the-art H_2-selective membrane (polyimide) described in Example 3 with a H_2 permeance of 100 GPU, a H_2/CO_2 selectivity of 10, and a H_2/CO selectivity of 100, and this process yields the product gas (permeate) at 1 atm (without the use of a sweep gas). The membrane area is 45 ft^2, and the product gas (permeate) contains 92.7% H_2, 7.3% CO_2, and 0.04% CO. Table 2 shows the comparison of the CO_2-selective membrane process of the present invention (Example 4) with the H_2-selective membrane process (Example 5). As shown in this table, the membrane process of this invention gives higher H_2 concentration (97.1% vs. 92.7%), i.e., lower combined concentration of carbon oxides (1.2% CO_2 and 1.7% CO vs. 7.3% CO_2 and 0.04% CO), much higher

product gas pressure (10 atm vs. 1 atm), greater H_2 recovery (83% vs. 80%), and less membrane area required (17 ft^2 vs. 45 ft^2) than the H_2-selective membrane process. In addition, the product gas of the former process with a lower combined concentration of carbon oxides is suitable for methanation to yield a desirable fuel cell fuel without carbon oxides, whereas the product gas of the latter process has too much CO_2 to be practically suitable for methanation. Thus, the process of this invention is again more effective and advantageous than the H_2-selective membrane process.

Table 2

Comparison of the CO_2-Selective Membrane Process with a H_2-Selective Membrane Process for Purification of a Reformed Gas without Containing N_2*

Process	Product Gas Composition (mole %) H_2	CO_2	CO	Total Product Gas Pressure (atm)	H_2 Recovery (%)	Membrane Area (ft^2)
CO_2-Selective Membrane Process, This Invention (Example 1)	97.1	1.2	1.7	10	83	17
H_2-Selective Membrane Process (Example 3)	92.7	7.3	0.04	1	80	45

*The reformed gas contains 74.9% H_2, 24% CO_2, and 1.1% CO at total pressure of 10 atm.

Example 6: Synthesis of 50 wt% Tetramethylammonium Fluoride Salt and 50 wt% Polyvinylalcohol Membrane

To 18.65 g of water was added 3.0 g of polyvinylalcohol (PVA) with stirring and heating at about 75°C until a clear solution of the polymer was obtained. Separately, 5.32 g of a tetramethylammonium fluoride salt with 4

H_2O ($(CH_3)_4NF \cdot 4\ H_2O$), which contained 3.0 g of tetramethylammonium fluoride salt, was dissolved in 5 g of water. This solution was added to the PVA solution with stirring for about 15 minutes to otain a clear, homogeneous solution. The resulting solution was then centrifuged while cooling for about 30 minutes. Following centrifugation, a membrane was knife-cast with a gap setting of 8 mils onto a support of microporous polytetrafluoroethylene. Water was allowed to evaporate from the membrane overnight in a nitrogen box at ambient conditions. The membrane was then heated in an oven at 90°C for 5 hours. The resulting membrane comprised about 60 wt% tetramethylammonium fluoride salt and 50 wt% polyvinylaclohol on the microporous polytetrafluoroethylene support, and had a thickness of 49 microns (exclusive of the support).

Example 7: Permeation Measurement of Membrane of Example 6

In the permeation measurement to evaluate the separation factor (selectivity) of CO_2 vs. H_2 and the permeability of CO_2, the membrane was placed in a permeation cell comprising the first compartment for contacting a feed stream against the upstream side of the membrane and the second compartment for withdrawing the permeate from the downstream side of the membrane. The active membrane area in the cell was 63.62 cm^2. A feed gas comprising 75% H_2 and 25% CO_2 under a total pressure of about 3 atm at ambient temperature (23°C) was contacted against the membrane at a flow rate of 120 cm^3/min. The permeate was swept by nitrogen under a pressure of about 1 atm and a total flow rate of 50.9 cm^3/min for the permeate/nitrogen stream. Both the feed and the sweep streams were humidified by bubbling through deionized water prior to contacting the membrane.

For the membrane of Example 6 comprising 50 wt% tetramethylammonium fluoride salt and 50 wt% polyvinylalcohol, the CO_2/H_2 selectivity result obtained was 19, and the C_2 permeability was 348 Barrers.

As shown in Example 7, the membrane of this invention may be employed for removal of CO_2 from a CO_2-containing gas, e.g., a reformed gas. The use of the membrane composition in the CO_2-selective membrane process of the present invention for the purification of a reformed gas for a fuel cell vehicle has been described in Example 4.

CLAIMS:

1. A process to purify a fuel feedstream comprising:

(a) reforming said fuel feedstream

(b) separating CO_2 from the fuel feedstream with a nonporous, CO_2 selectively permeable membrane so that CO_2 is selectively removed from the fuel feedstream leaving an enriched feedstream in hydrogen.

2. The process of claim 1 further comprising the step of water gas shift reaction for the fuel feedstream.

3. The process of claim 1 wherein the reforming step and the separating step are performed concurrently.

4. The process of claim 1 wherein reforming step and the separating step are performed sequentially.

5. The process of claim 2 wherein the water gas shift reaction step and the separating step are performed concurrently.

6. The process of claim 2 wherein the water gas shift reaction step and the separating step are performed sequentially.

7. The process of claim 1 further comprising the step of methanating said enriched feedstream.

8. The process of claim 2 further comprising the step of methanating said enriched feedstream.

9. A system for converting a fuel feedstream to a hydrogen rich and CO_x (CO_2 and CO) deficient feedstream comprising a reformer, a water gas shifter and CO_2-selective membrane reactor, and a methanator.

10. A system for converting a fuel feedstream to a hydrogen rich and CO_x deficient feedstream comprising a reformer, a water gas shifter, a CO_2-selective membrane separator, and a methanator.

11. A system for converting a fuel feedstream to a hydrogen rich and CO_x deficient feedstream comprising a reformer and CO_2-selective membrane reactor, and a methanator.

12. A system for converting a carbon fuel feedstream to a hydrogen rich and Co_x deficient feedstream comprising of a reformer, a CO_2-selective membrane separator, and a methanator.

13. The system of claim 9 further comprising a fuel cell.

14. The system of claim 10 further comprising a fuel cell.

15. The system of claim 11 further comprising a fuel cell.

16. The system of claim 12 further comprising a fuel cell.

17. The system of claim 13 wherein said system is on-board a vehicle that is driven by said fuel cell.

18. The system of claim 14 wherein said system is on-board a vehicle that is driven by said fuel cell.

19. The system of claim 15 wherein said system is on-board a vehicle that is driven by said fuel cell.

20. The system of claim 16 wherein said system is on-board a vehicle that is driven by said fuel cell.

21. A composition comprising:

a hydrophilic polymer and at least one ammonium halide salt, the ammonium halide salt being present in an amount ranging from about 10 to about 80 wt% based on the total weight of the composition, wherein the ammonium halide salt is selected from ammonium halide salts having the formulae and mixtures thereof:

$$(R)_4 N^+ X^-$$

wherein R is hydrogen or an alkyl group having from 1 to 4 carbon atoms and X is a halide, the halide being selected from the group consisting of fluoride, chloride, bromide, iodide, and mixtures thereof.

22. The composition of claim 17 wherein the hydrophilic polymer is selected from the group consisting of polyvinylalcohol, polyvinylpyrrolidone, polyethyleneoxide, polypropyleneoxide, polyacrylamide, polyvinylacetate, blends and copoloymers thereof.

23. The composition of claim 21 wherein the polymer is polyvinylalcohol.

24. The composition of claim 21 including from about 1 to about 20 wt% of a cross-linking agent based on the total weight of composition.

25. The composition of claim 22 wherein the cross-linking agent is selected from the group consisting of formaldehyde, divinyl sulfone, toluene disocyanate, glyoxal, glutaraldehyde, trimethylol melamine, terephthaladehyde, epichlorohydrin, vinyl acrylate, and maleic anhydride.

26. The composition of claim 21 wherein the ammonium halide salt is tetramethylammonium fluoride salt.

27. A nonporous membrane formed from the composition of claim 21.

28. A method for producing a nonporous membrane having properties sufficient to enable separation of CO_2 from a gaseous stream containing CO_2, the method comprising:

forming a casting solution of a solvent, a hydrophylic polymer and at least one ammonium halide salt, the ammonium halide salt being present in an amount ranging from about 10 to about 80 wt% based on the total weight of polymer and salt;

casting the solution on a substrate; and

evaporating the solvent whereby a nonporous membrane is formed.

29. The method of claim 28 including adding a cross-linking agent to the polymer solution.

30. The process of claim 1 wherein the membrane of claim 27 is used.

31. The process of claim 2 wherein the membrane of claim 27 is employed.

32. The process of claim 3 wherein the membrane of claim 27 is utilized.

33. The process of claim 4 wherein the membrane of claim 27 is used.

34. The process of claim 5 wherein the membrane of claim 27 is employed.

35. The process of claim 6 wherein the membrane of claim 27 is utilized.

36. The process of claim 7 wherein the membrane of claim 27 is used.

37. The process of claim 8 wherein the membrane of claim 27 is employed.

Figure 1

FLOW DIAGRAM FOR THE FIRST CASE OF THE CO_2-SELECTIVE MEMBRANE PROCESS OF THE PRESENT INVENTION

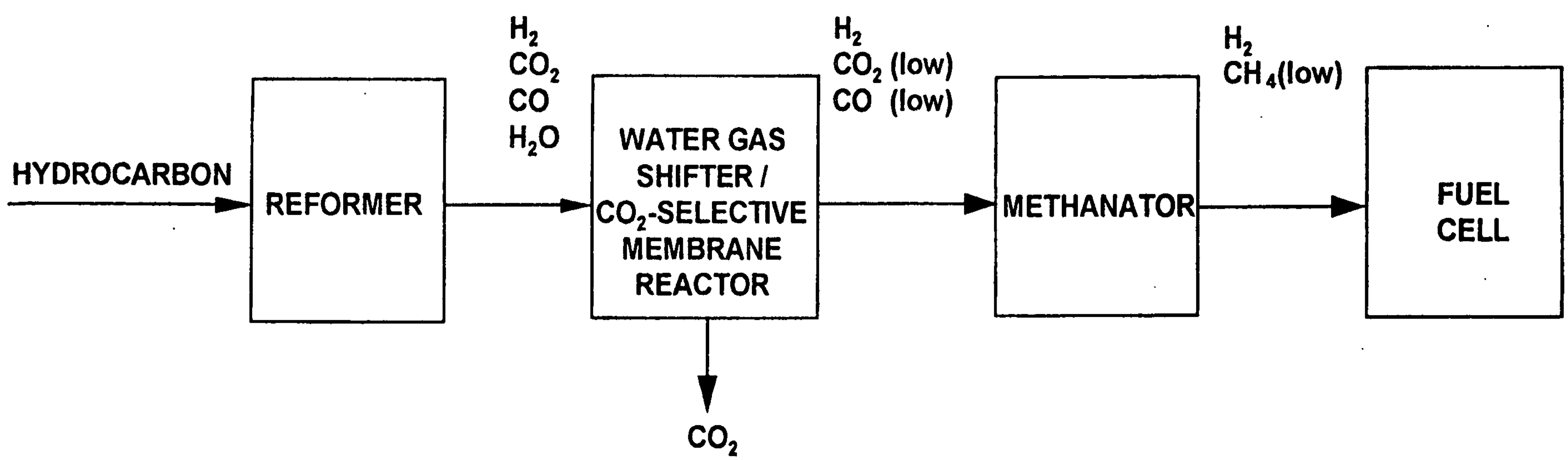


Figure 2

FLOW DIAGRAM FOR THE SECOND CASE OF THE CO_2-SELECTIVE MEMBRANE PROCESS OF THE PRESENT INVENTION

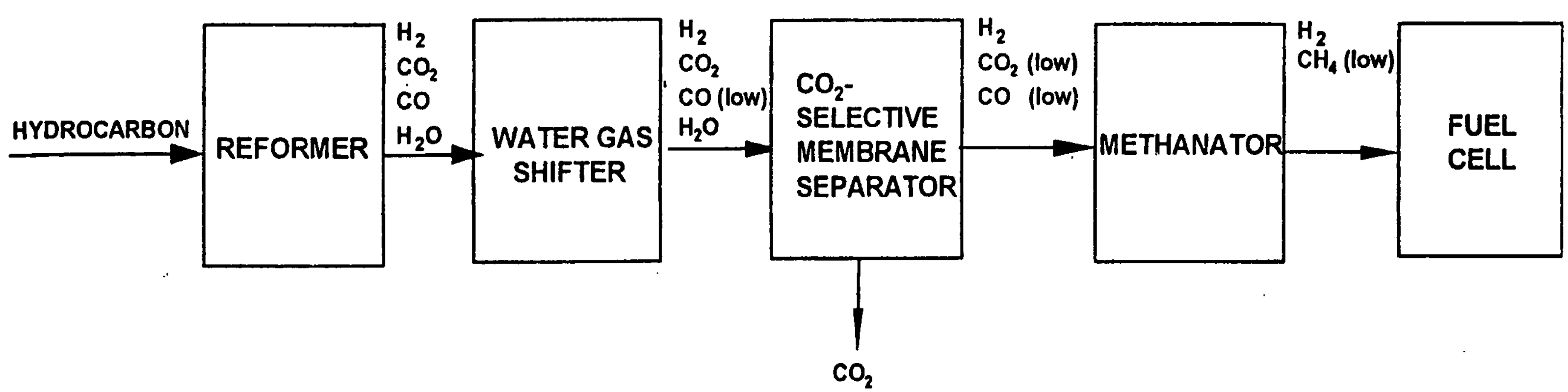


Figure 3

FLOW DIAGRAM FOR THE THIRD CASE OF THE CO_2-SELECTIVE MEMBRANE PROCESS OF THE PRESENT INVENTION

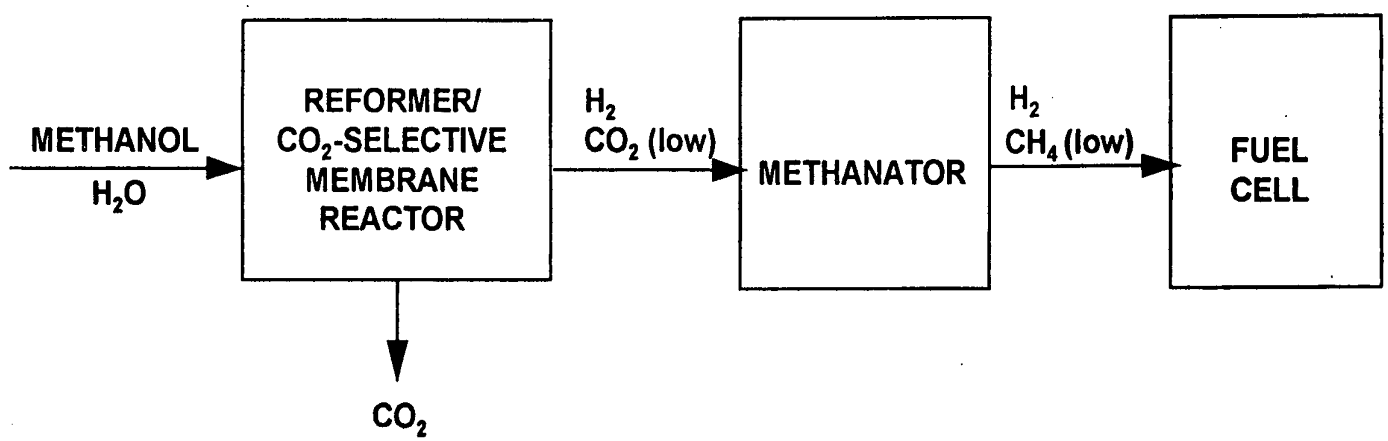
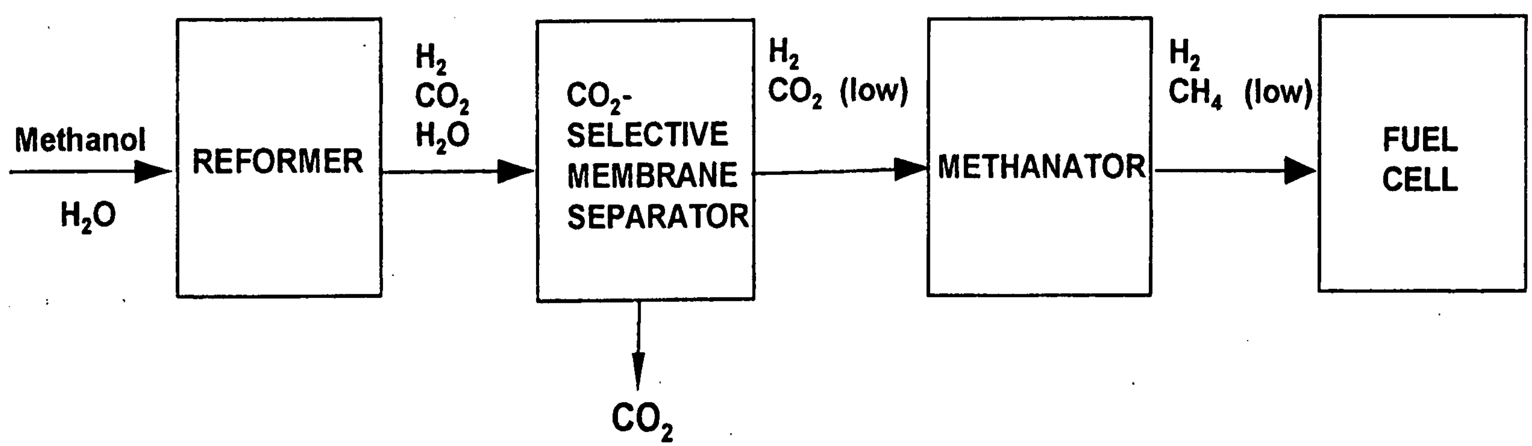


Figure 4

FLOW DIAGRAM FOR THE FOURTH CASE OF THE CO_2-SELECTIVE MEMBRANE PROCESS OF THE PRESENT INVENTION



INTERNATIONAL SEARCH REPORT

International application No.
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A. CLASSIFICATION OF SUBJECT MATTER
IPC(6) : B01D 53/22
US CL :48/198.3; 95/51; 96/4
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED
Minimum documentation searched (classification system followed by classification symbols)
U.S. : 48/198.3; 95/51; 96/4

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 5,445,669 A (NAKABAYASHI et al.) 29 August 1995, see entire document.	1-37

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
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30 OCT 1998

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